

2,5-Diacyl-1,4-Dimethylbenzenes—Examples of Bisphotoenol Equivalents

(NASA-TM-89836) THE
2,5-DIACYL-1,4-DIMETHYLBENZENES: EXAMPLES OF
BISPHOTOENOL EQUIVALENTS (NASA) 15 p
Avail: NTIS HC A02/MF A01 CSCL 07A

N87-22005

Unclas
H1/23 0071123

Michael A. Meador
Lewis Research Center
Cleveland, Ohio

Prepared for the
194th National Meeting of the American Chemical Society
New Orleans, Louisiana, August 30—September 4, 1987

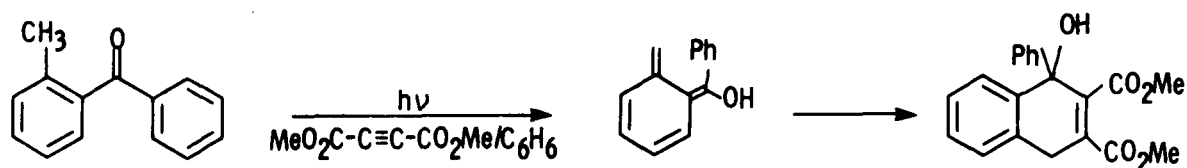


2,5-DIACYL-1,4-DIMETHYLBENZENES - EXAMPLES OF BISPHOTOENOL EQUIVALENTS

Michael A. Meador
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

INTRODUCTION

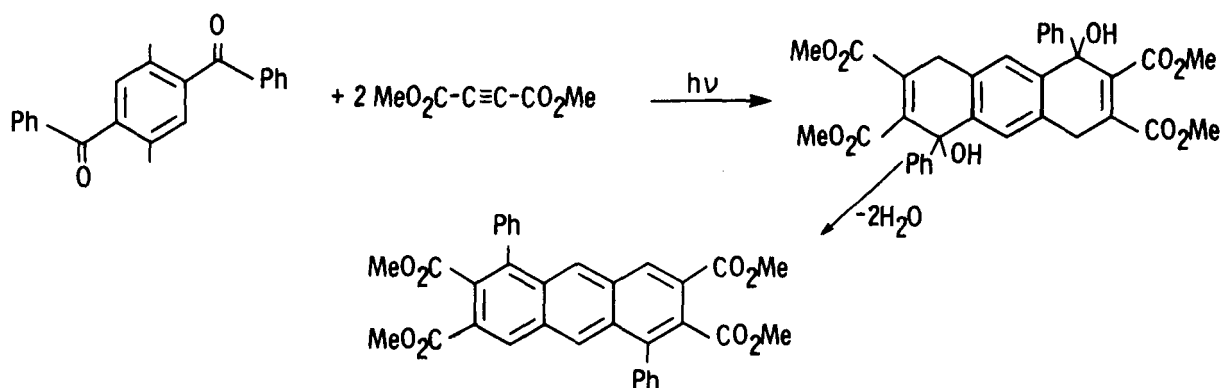
In 1961 Yang and Rivas (ref. 1) reported that photolysis of o-methylbenzophenone afforded a hydroxy-o-quinodimethane which could be trapped with dimethyl acetylenedicarboxylate to provide the corresponding tetralin diester. Since then, the photoenolization of o-methylphenyl ketones has been studied from both mechanistic (ref. 2) and synthetic (ref. 3) perspectives.



This reaction occurs from the triplet manifold and involves abstraction of an o-methyl hydrogen by the carbonyl oxygen to afford a triplet 1,4-biradical (Scheme 1). Decay of this triplet biradical (via intersystem crossing) yields two isomeric photoenols, designated E- and Z-corresponding to the relative positions of the hydroxyl and methylene groups. The hydroxyl group in the Z-photoenol is properly aligned to permit reabstraction of the hydroxyl hydrogen by the exo-methylene carbon, via a six-centered transition state. For this reason the Z-photoenol is extremely short-lived (ref. 4) (a nanosecond or less). Since this reabstraction is not possible in the E-isomer it is fairly long-lived (on the order of a few microseconds in some solvents).

This long lifetime permits the E-photoenol to participate in common ground state chemical reactions. In particular, since the photoenol is a conjugated diene, it can undergo Diels Alder cycloadditions to yield fused ring systems.

A number of examples of Diels-Alder cycloadditions of various photoenols with a variety of dieneophiles have been published (ref. 3). However, all of the work to date has concentrated on the chemistry of compounds capable of forming only one photoenol per molecule (photoenol equivalents). The research described in this paper was concerned with whether the same chemistry could be applied to compounds having two enolizable sites per molecule (bisphotoenol equivalents). Furthermore, the Diels-Alder trapping of these photoenols could be applied to the synthesis of highly substituted anthracenes which might be difficult or impossible to prepare by other means.



Currently, the best approaches to highly substituted anthracenes involve some type of Diels-Alder cycloaddition followed by aromatization. The overall yields for these methods are quite good, and a number of different Diels-Alder schemes are available providing a variety of substituted anthracenes (Scheme 2).

Substituted furans and pyrroles have been reacted with bisaryne equivalents to provide the corresponding 1,4,5,8-tetrahydroanthracene-1,4,5,8-bisepoxides and -bisimines (ref. 5). Removal of the oxygen bridge of the bisepoxides is typically accomplished with low-valent metal species such as iron (ref. 6) or titanium (ref. 7). The nitrogen bridge of the bisimines is usually removed by pyrolysis under vacuum (ref. 5). While this method provides a number of highly substituted anthracenes in good overall yield it does have its limitations. In particular the method in which the aryne is generated strongly dictates the types of furans or pyrroles that can be used. For example, generation of the aryne by treatment of a tetrahalobenzene with an organolithium reagent limits the choice of furan or pyrrole to those compatible with organolithium reagents. This problem can be avoided by the use of other diaryne equivalents, but many of these are difficult to synthesize (ref. 8).

Another Diels-Alder approach involves the cycloaddition of a substituted 1,5-diphenylisobenzofuran with an oxabicyclo-[2.2.1]-5-heptene derivative (ref. 9). While this method avoids the problems associated with the bisaryne approach, the overall synthesis is quite lengthy.

EXPERIMENTAL

2,5-Dibromo-1,4-dimethylbenzene, phenylmagnesium bromide, and all dienophiles were obtained from Aldrich Chemical Co. and used as received. Benzene (hplc grade) was obtained from Fisher Scientific and used as received. Sodium sulfate was used as the drying agent for all reactions.

Melting points were measured on a Thomas Hoover apparatus and are uncorrected. ^1H NMR were recorded on either a Varian FT-80A or a Varian XL-200 spectrometer. ^{13}C NMR spectra were recorded on a Varian XL200 spectrometer.

Unless otherwise indicated, CDCl_3 was used as a solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million (δ) relative to TMS.

2,5-Dicyano-1,4-dimethylbenzene (1). - A mixture of 26.2 g of 2,5-Dibromo-1,4-dimethylbenzene (0.10 mol) and 18.9 g of CuCN (0.22 mol) in 300 mL dimethylformamide was refluxed under nitrogen for 6 hr. The mixture was then poured hot into a stirred solution of 20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 50 mL concentrated HCl in 250 mL distilled water. The resulting lime green suspension was stirred at 60 °C for 20 min. It was then cooled to room temperature and extracted three times with 150 mL portions of benzene. The benzene extracts were combined and neutralized with 400 mL of a saturated aqueous NaHCO_3 solution. The organic phase was dried and the solvent removed under vacuum to afford a cream colored solid. Recrystallization of this solid from ethanol afforded 15.4 g of 1 as off-white needles (98.7 percent), mp 190-192 °C. $^1\text{H-NMR}$ δ 2.55 (s, 6H), 7.56 (s, 2H); $^{13}\text{C-NMR}$ δ 19.81, 116.9, 133.8, 139.9.

2,5-Dibenzoyl-1,4-dimethylbenzene (2). - To a stirred solution of 16.0 g 1 (0.103 mol) in 400 mL freshly distilled tetrahydrofuran under nitrogen was added dropwise 75 mL of a 3.0 M solution of phenylmagnesium bromide (0.226 mol) in diethyl ether. The resulting mixture was refluxed under nitrogen for 18 hr. The reaction mixture was then allowed to cool to room temperature and poured into 400 mL of a saturated aqueous solution of NH_4Cl . The two phases were separated and the aqueous phase extracted twice with 150 mL portions of diethyl ether. The organic extracts were combined and dried. The solvent was removed under vacuum to afford a yellow-green oil. This oil was dissolved in a solution of 200 mL concentrated HCl in 200 mL distilled water and refluxed for 18 hr under nitrogen. The reaction mixture was then cooled to room temperature and extracted three times with 150 mL portions of diethyl ether. The ether extracts were combined and washed twice with 200 mL portions of a 5 percent aqueous NaOH solution. The ether solution was dried and the solvent removed under vacuum to afford 25.0 g of 2 (77 percent) as an off-white solid. Recrystallization of this solid from hot ethanol afforded pure 2 as cream colored needles, mp 162-163 °C. $^1\text{H-NMR}$ δ 2.27 (s, 6H), 7.91-7.22 (m, 12H); $^{13}\text{C-NMR}$ δ 19.33, 128.6, 130.1, 130.4, 133.5, 137.2, 140.4, 198.2.

General Procedure for the Photoaddition. - Typically 500 mL of a benzene solution of 2 and dienophile was vigorously degassed under nitrogen for 1 hr. The stirred solution was then irradiated under nitrogen for 18 hr using a 450 W medium pressure Hg lamp (Hanovia) equipped with a uranium glass filter. The benzene was removed under vacuum to afford crude photoadduct.

Tetramethyl-1,5-dihydroxy-1,5-diphenyl-1,4,5,8-tetrahydroanthracene-2,3,6,7-tetracarboxylate (3). - A 250 mL benzene solution of 0.79 g 2 (2.52 mmol, 0.01 M) and 3.55 g dimethyl acetylenedicarboxylate (25.0 mmol, 0.1 M) was irradiated for 18 h. The solvent was removed under vacuum to afford a yellow oil which was dissolved in 10 mL benzene and purified by flash chromatography (Baker Silica Gel, 40 μm , ethyl acetate/cyclohexane 1:4) to afford pure 0.8 g 3 (53 percent) as a cream colored solid, mp 268-270 °C (dec). $^1\text{H-NMR}$ δ 1.56 (br s, 1H), 3.76 (s, 3H), 3.8 (s, 3H), 3.60-4.11 (AB quartet, $J=\text{Hz}$), 7.2-7.4 (m, 6H); $^{13}\text{C-NMR}$ δ 30.67, 52.59, 52.42, 74.06, 125.5, 126.2, 127.4, 128.0, 128.3, 129.5, 132.2, 138.6, 144.6, 166.9, 167.8.

Tetramethyl 2,3-Dihydroxy-2,3-diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,5,7-tetracarboxylate (4). - A 500 mL benzene solution

of 2 (2.0 g, 6.4 mmol, 0.013 M) and 2.03 g dimethyl fumarate (14.1 mmol, 0.028 M) was irradiated under nitrogen for 20 hr. The solvent was removed and the resulting yellow residue recrystallized from methanol to afford 3.1 g of 4 (80.4 percent) as a cream colored solid, mp 294-295 °C; ^1H NMR δ 2.83-3.66 (m, 8H), 3.39 (s, 6H), 3.66 (s, 6H), 7.36-7.27 (m, 10H); ^{13}C NMR δ 31.95, 39.59, 51.96, 52.18, 54.29, 126.4, 127.4, 127.9, 129.6, 132.5, 139.6, 144.3, 173.8, 174.8.

Dimethyl 1,5-Dihydroxy-1,5-diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene-2,6-dicarboxylate (5). - A 500 mL benzene solution of 2 (4.0 g, 12.8 mmol, 0.013 M) and 2.6 mL of methyl acrylate (28.0 mmol, 0.056 M) was irradiated under nitrogen for 6 hr. The benzene was removed under vacuum and the resulting white residue triturated with methanol to afford 1.5 g of a white powder (isomer 5a, 25 percent), mp 295-296 °C. The methanol was removed from the mother liquor and the residue recrystallized from ethanol to afford 3.3 g of isomer 5b (56 percent), mp 130-132 °C. 5a ^1H -NMR δ 1.98-1.59 (m, 2H), 2.40-2.23 (m, 2H), 2.77-2.57 (m, 4H), 3.10, 3.16 (d, $J=2.8\text{Hz}$, 2H), 3.52 (s, 6H), 5.01 (s, 2H), 6.68 (s, 2H), 7.25-7.31 (m, 10H); ^{13}C -NMR δ 23.00, 28.32, 51.87, 52.04, 75.17, 126.6, 126.9, 127.8, 129.4, 133.8, 139.9, 146.3, 176.2. 5b ^1H -NMR δ 1.70-2.00 (m, 2H), 2.10-2.40 (m, 2H), 2.75-2.81 (m, 4H), 3.11, 3.16 (d, $J=3.0\text{Hz}$, 2H), 3.54 (s, 6H), 4.82 (s, 2H, OH), 6.79 (s, 2H), 7.25-7.36 (m, 10H).

Dimethyl 4-Hydroxy-4-phenyl-6-methyl-7-benzoyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (6). - A 250 mL benzene solution of 2 (2.6 g, 8.33 mmol, 0.033 M) and 1.2 g dimethyl fumarate (8.33 mmol, 0.033 M) was irradiated under nitrogen for 23 hr. The solvent was removed under vacuum and the residue recrystallized from methanol to afford 1.3 g 6 (34 percent) as a cream colored solid, mp 176-178 °C. ^1H NMR δ 3.18-3.75 (m, 4H), 3.43 (s, 3H), 3.72 (s, 3H), 4.55 (s, 1H, -OH), 6.73 (s, 1H), 7.14 (s, 1H), 7.27-7.83 (m, 10H); ^{13}C NMR 19.52, 31.80, 39.64, 51.97, 52.24, 54.44, 75.85, 126.3, 127.4, 128.0, 128.4, 128.5, 128.6, 130.1, 130.9, 131.9, 133.3, 135.1, 137.4, 138.8, 141.3, 144.3, 173.9, 174.5.

Trimethyl 1,5-Dihydroxy-1,5-diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6-tricarboxylate (7). - A 250 mL benzene solution of 0.87 g of 6 (1.90 mmol, 0.0076 M) and 0.26 mL methyl acrylate (2.89 mmol, 0.012 M) was irradiated under nitrogen for 23 hr. The solvent was removed under vacuum to afford 1.0 g of 7 (93 percent) as a pale yellow solid. Recrystallization from hot ethanol afforded pure 7 as long white needles, mp 155-156.5 °C. ^1H NMR δ 1.88-3.39 (m, 9H), 3.39 (s, 3H), 3.53 (s, 3H), 3.66 (s, 3H), 4.43 (s, 1H), 5.05 (s, 1H), 6.57 (s, 1H), 6.72 (s, 1H), 7.27-7.36 (m, 10H); ^{13}C NMR δ 22.91, 28.33, 32.04, 39.70, 51.90, 52.15, 54.52, 75.08, 76.00, 126.5, 126.6, 127.1, 127.3, 127.8, 129.5, 129.6, 132.0, 134.3, 138.9, 140.5, 144.6, 146.1, 174.0, 174.9, 176.1.

Tetramethyl 1,5-Diphenyl-3,4,7,8-tetrahydroanthracene-2,3,6,7-tetracarboxylate (8). - A solution of 0.25 g 4 (0.42 mmol) and 1.0 mL concentrated HCl in 50 mL benzene was refluxed under nitrogen for 24 hr. The solution was cooled to room temperature and neutralized with 300 mL saturated aqueous NaHCO_3 . The layers were separated and the organic phase dried. The solvent was removed under vacuum to afford 0.23 g of 8 (100 percent), mp 216-218 °C. ^1H -NMR δ 3.07-3.04 (d, $J=6.5\text{Hz}$, 4H), 3.44, 3.63 (s, 12H), 3.86-3.92 (t, $J=6.5\text{Hz}$, 2H), 6.59 (s, 2H), 7.51-7.19 (m, 10H); ^{13}C -NMR δ

31.16, 41.64, 51.54, 52.30, 125.8, 127.5, 127.6, 128.1, 128.3, 128.6, 132.8, 135.2, 138.3, 146.4, 168.0, 173.3.

Dimethyl 1,5-Diphenyl-3,4,7,8-tetrahydroanthracene-2,6-dicarboxylate (9).

- A solution of 0.3 g 5 (0.62 mmol) and 1.0 mL concentrated HCl in 50 mL benzene was refluxed under nitrogen for 24 hr. The solution was then cooled to room temperature and extracted with 300 mL saturated aqueous NaHCO₃. The organic phase was dried and the solvent removed under vacuum to afford 0.28 g 9 as a white powder, mp 246.5-247.5 °C. ¹H NMR δ 2.66 (br sing, 8H), 3.45 (s, 6H), 6.58 (s, 2H), 7.00-7.25 (m, 4H), 7.35-7.49 (m, 6H); ¹³C NMR δ 25.41, 27.67, 51.30, 126.8, 127.4, 128.1, 128.3, 128.7, 135.1, 135.5, 139.0, 144.6, 169.3.

Trimethyl-1,5-diphenyl-3,4,7,8-tetrahydroanthracene-2,3,6-tricarboxylate (10). - A solution of 1.4 g 8 (2.57 mmol) in 25 mL acetic anhydride and 2 mL conc. HCl was refluxed under nitrogen for 2 hr. The solution was then poured over 200 mL crushed ice and the tan solid removed by filtration once the ice had melted. This solid was recrystallized from methanol to afford 0.85 g 10 (65 percent) as a cream colored solid, mp 163-164 °C. ¹H-NMR δ 2.65 (br s, 4H), 3.06 (d, J=6Hz, 2H), 3.42, 3.43, 3.63 (s's, 9H), 3.88 (t, J=6Hz, 1H), 6.58 (s, 2H), 7.07-7.46 (m, 10H); ¹³C-NMR δ 25.34, 27.65, 31.15, 41.61, 51.33, 51.51, 52.29, 125.3, 126.9, 127.36, 127.4, 127.6, 128.0, 128.1, 128.6, 128.7, 132.4, 134.6, 135.5, 136.1, 138.6, 138.8, 144.3, 168.0, 169.2, 173.4.

Tetramethyl-1,5-Diphenylanthracene-2,3,6,7-tetracarboxylate (11). -

Method A. A solution of 2.0 g 3 (3.34 mmol) and 5 mL concentrated HCl in 25 mL acetic anhydride was refluxed under nitrogen for 20 hr. The solution was then cooled to room temperature and poured into 250 mL distilled water. The resultant yellow precipitate was filtered and recrystallized from ethanol to afford 1.5 g of 11 (80 percent) as a bright yellow solid, mp 334-335 °C. ¹H-NMR δ 3.60, 3.92 (s, 12H), 7.25-7.55 (m, 10H), 8.27, 8.63 (s, 4H); ¹³C-NMR δ 52.24, 52.69, 125.3, 128.3, 128.4, 129.0, 130.2, 130.8, 131.6, 132.3, 133.0, 136.1, 139.0, 165.9, 168.9.

Method B. A solution of 1.0 g 8 (1.77 mmol) and 1.0 g of sulfur (31.3 g-atom) in 10 mL diphenyl ether was refluxed for 4 hr (until evolution of hydrogen sulfide had ceased.) The solution was then allowed to cool to room temperature. Methylene chloride (200 mL) was added and the mixture filtered to remove excess sulfur. The methylene chloride was removed under vacuum, and 200 mL diethyl ether was added to the brown residue. Immediately an orange precipitate formed which was filtered to provide 0.8 g of 11 (80 percent). The melting point and ¹H-NMR spectrum were identical to that of the material prepared by method A.

Dimethyl-1,5-Diphenylanthracene-2,6-dicarboxylate (12). - A suspension of 2.0 g 6 (4.44 mmol) and 2.0 g sulfur (62.5 g-atom) in 15 mL diphenyl ether was refluxed for 4 hr (until no further evolution of hydrogen sulfide was observed). This mixture was then cooled to room temperature, 200 mL methylene chloride added, and the solution filtered. The methylene chloride was removed under vacuum and 100 mL methanol added. This solution was cooled in an ice bath and filtered to afford 1.7 g 12 (86.6 percent) as bright yellow needles, mp 210-212 °C. ¹H-NMR δ 3.62 (s, 6H), 7.2-7.9 (m, 10H), 8.19 (s, 2H); ¹³C-NMR δ 52.00, 124.8, 127.6, 128.1, 128.2, 128.7, 128.9, 129.5, 129.6, 132.4, 138.7, 141.7, 168.5.

Trimethyl-1,5-diphenylanthracene-2,3,6-tricarboxylate (13). - A suspension of 0.5 g 10 (0.98 mmol) and 0.5 g sulfur (0.015 g-atom) in 5 ml diphenyl ether was refluxed for 2 hr until no further evolution of hydrogen sulfide was observed. The reaction mixture was cooled to room temperature and methanol added to afford 0.25 g 13 (50 percent) as orange-yellow needles, mp 206-208 °C. ¹H-NMR δ 3.61, 3.63, 3.92 (s, 9H), 7.25-7.57 (m, 10H), 7.89 (s, 2H), 8.14, 8.33, 8.63 (s, 3H); ¹³C-NMR δ 52.07, 52.17, 52.59, 124.3, 126.0, 126.5, 127.8, 128.2, 128.5, 129.6, 130.3, 130.7, 131.8, 132.3, 133.4, 133.9, 136.5, 138.4, 138.6, 142.1, 166.1, 168.3, 169.1.

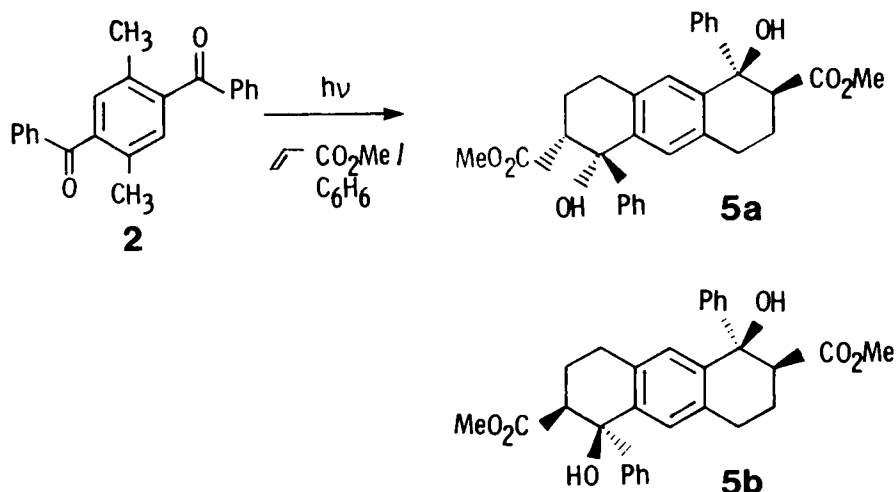
RESULTS AND DISCUSSION

The yields for all products and reactions are reported in table 1. In general, the Diels-Alder trapping of both photoenols derived from 2 proceeded in fair to good yields (34 to 93 percent.) In all but one case, a nearly stoichiometric amount of dienophile (2.2 equivalents) was used. However, in the case of bisadduct 3, a large excess of dimethyl acetylenedicarboxylate was required since both it and the photoproduct, which is also a good dienophile, are in competition for photoenols. Trapping of photoenols derived from 2 with bisadduct 3 would result in polymerization. In fact, if dimethyl acetylenedicarboxylate is not used in large excess (ten equivalents) the yields of 3 are significantly lower than 53 percent. For example, if four equivalents are used, the bis adduct is formed in only 13 yield (the other products are 26 percent monoadduct, and 61 percent polymer.) No bisadduct is formed if two equivalents of dimethyl acetylenedicarboxylate are used.

Formation of bisadduct is a step-wise process proceeding through an initially formed monoadduct as depicted in Scheme 3. This is confirmed by the photolysis of 2 in the presence of only one equivalent of dimethyl fumarate to afford monoadduct 6 in 34 percent yield, in close agreement with the statistically predicted yield. Monoadduct 6 can also be used to prepare unsymmetrically substituted bisadducts, such as triester 7.

Photoadduct formation is regiospecific. For example, photolysis of 2 and methyl acrylate affords only 5, where the OH and CO₂CH₃ are on adjacent carbons. While structural assignment based on ¹H NMR was difficult, dehydration of 5 produced only 9 and confirmed the structure of octahydroanthracene 5. This regiochemistry is in agreement with the results reported for trapping other photoenols (refs. 3(b) to (d) in which the OH directs the ester α to itself. This directing effect should also result in a cis orientation of the hydroxyl and carbomethoxy groups (ref. 3(c), although it is not clear from simple ¹H NMR that this orientation is obtained in the bisadducts reported here.

Since this reaction is stepwise, its overall stereochemistry is complicated by the fact that there are two independent reaction sites on 2. Assuming the primary stereochemistry as discussed above, a pair of diastereomers should be formed for each photoadduct—one with hydroxyl groups syn and one with them anti. This is in fact the case. For example, irradiation of 2 with slightly more than two equivalents of methyl acrylate produced two isomers of the desired bisadduct 5. Isomer 5a is formed in the lower yield and is presumed to be the anti isomer on the basis of its melting point relative to that of the less symmetric syn isomer 5b. However, exact structural confirmation is not possible from the data obtained to date.



All of the photoadducts smoothly dehydrated to the corresponding tetrahydroanthracenes using hydrochloric acid in refluxing acetic anhydride or benzene. However, aromatization of these tetrahydroanthracenes proved to be somewhat delicate. Dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) would only proceed in refluxing dioxane saturated with HCl gas to promote dehydrogenation through the enol of the ester (ref. 10). Unfortunately some hydrolysis of the ester also occurred giving rise to carboxylic acids which were difficult to separate from the hydroquinone of DDQ. Yields from DDQ dehydrogenations were 25 percent at best for any of the bisadducts. Instead, the use of sulfur in refluxing diphenyl ether provided the desired anthracenes in roughly 80 percent yields.

This cycloaddition was also attempted with 2,5-diacetyl-1,4-dimethylbenzene, **14**, in an effort to test the generality of this method with other diacyl-*p*-xylenes. Unfortunately, irradiation of **14** in the presence of any of the dienophiles used with **2** did not give any photoproducts. Irradiation of a CD_3OD solution of **14** in an NMR tube resulted in deuterium incorporation in both *o*-methyl groups and confirmed that **14** was undergoing photoenolization. Pfau and coworkers (ref. 11) have reported similar difficulty in the trapping of *o*-methylacetophenone photoenol with a number of dienophiles. Rivas (ref. 12), however, has reported the trapping of this photoenol with dimethyl acetylenedicarboxylate in 30 yield.

Recently, Charlton and Durst (ref. 13) published a series of articles dealing with the trapping of photoenols from *o*-methylphenyl ketones and benzaldehydes with sulfur dioxide (Scheme 4). Ethers and acetates of the α -hydroxysulfone photoadducts can be pyrolyzed (at 150–220 °C) to the corresponding 1-hydroxy-*o*-quinodimethanes (ground state photoenols). Alternatively, these α -hydroxysulfones can be reduced with sodium borohydride and treated with hydrochloric acid to produce cyclic sulfinate esters (sultines) which decompose to *o*-quinodimethanes in refluxing cyclohexane. The authors have successfully trapped these *o*-quinodimethanes with dienophiles to afford substituted tetrahydronaphthalenes.

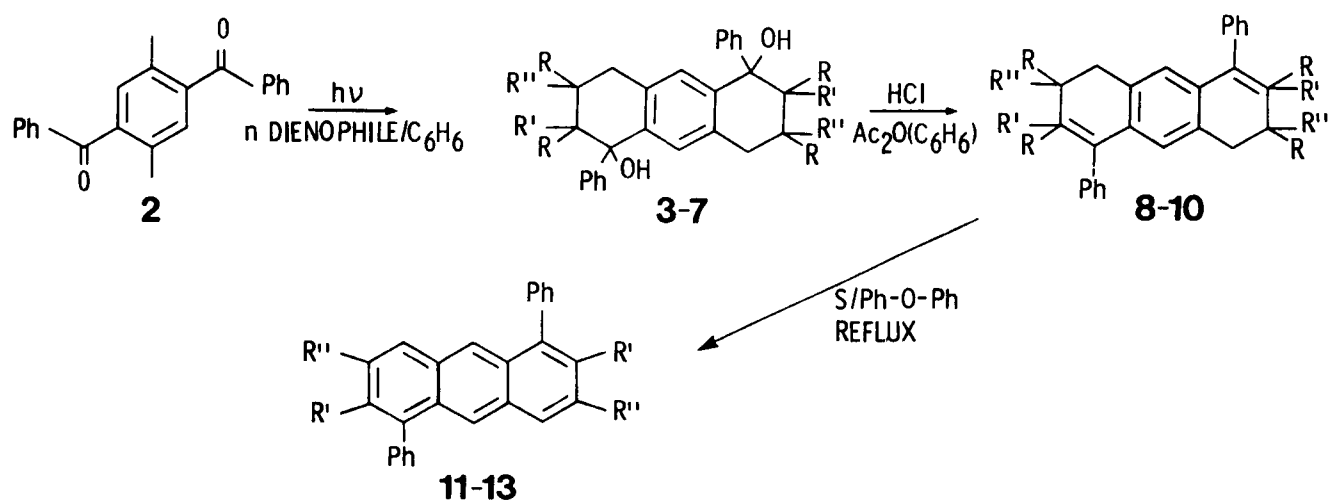
Photolysis of 14 in benzene saturated with sulfur dioxide afforded the desired bis-(α -hydroxysulfone), 15, in good yield (ref. 14) (60 percent). The trapping of o-quinodimethanes generated from 15 and its derivatives is currently under investigation.

The use of 2,5-dibenzoyl-1,4-dimethylbenzene as a bisphotoenol equivalent affords a number of substituted anthracenes in high yield. In addition to this, diketones such as 2 are easily prepared from Grignard reactions. Hence, this method provides an attractive approach to the synthesis of substituted anthracene precursors, with some limitations as discussed earlier. This work is being extended to other 2,5-diaroyl-1,4-dimethylbenzenes and the preparation of more highly substituted anthracenes.

REFERENCES

1. Yang, N.C.; Rivas, C. J. Am. Chem. Soc. 1961, 83, 2213.
2. (a) Zwicker, E.F.; Grossweiner, L.I.; Yang, N.C. J. Am. Chem. Soc. 1963, 85, 2671-2672.
 (b) Beckett, A.; Porter, G. Trans. Faraday Soc. 1963, 59, 2051-2057.
 (c) Porter, G.; Tchir, M.F. J. Chem. Soc. A 1971, 3772-3777.
 (d) Porter, G.; Tchir, M.F. J. Chem. Soc. D 1970, 1372-1373.
 (e) Wagner, P.J.; Chen, C.P. J. Am. Chem. Soc. 1976, 98, 239-241.
 (f) Haag, R.; Wirz, J.; Wagner, P.J. Helv. Chim. Acta. 1977, 60, 2595-2607.
 (g) Das, P.K.; Encinas, M.V.; Small, R.D., Jr.; Scaiano, J. C. J. Am. Chem. Soc. 1979, 101, 6965-6970.
 (h) Small, R.D., Jr.; Scaiano, J.C. J. Am. Chem. Soc. 1977, 99, 7713-7714.
3. (a) Sammes, P.G. Tetrahedron 1976, 32, 405-422.
 (b) Arnold, B.J.; Mellows, S.M.; Sammes, P.G. J. Chem. Soc. Perkins Trans. 1 1973, 1266-1270.
 Arnold, B.J.; Mellows, S.M.; Sammes, P.G.; Wallace, T.W. J. Chem. Soc. Perkins Trans. 1 1974, 401-409.
 (c) Block, E.; Stevenson, R. J. Chem. Soc. Perkins Trans. 1 1973, 308-313.
 (d) Pfau, M.; Combrisson, S.; Row, J.E., Jr.; Heindel, N.D. Tetrahedron 1978, 34, 3459-3468.
 Pfau, M.; Row, J.E., Jr.; Heindel, N.D. Tetrahedron 1978, 34, 3469-3473.
 (e) Amaro, A.; Carenno, M.C.; Farina, F. Tetrahedron Lett. 1979, 41, 3983-3986.
4. (a) Small, R.D., Jr.; Scaiano, J.C. J. Phys. Chem. 1977, 81, 2126-2131.
 (b) Scaiano, J.C. Tetrahedron 1982, 38, 819-824.
5. Hart, H.; Lai, C.; Nwokogu, G.; Shamoullian, S.; Teurstein, A.; Zlotogorski, C. J. Am. Chem. Soc. 1980, 102, 6649-6651.
6. Best, W.M.; Collins, P.A.; McCulloch, R.K.; Wege, D. Aust. J. Chem. 1982, 35, 843-848.
7. Hart, H.; Nwokogu, G. J. Org. Chem. 1981, 46, 1251-1255.
8. Hart, H.; Ok, D. J. Org. Chem. 1986, 51, 979-986.

- 9 Schmitz, C.; Aubry, J.M.; Rigaudy, J. Tetrahedron 1982, 38, 1425-1430.
10. Sarel, S.; Shalon, Y.; Yanuka, Y. J. Chem. Soc. D 1970, 80, 81-82.
11. Pfau, M.; Heindel, N.D.; Lemke, T.F. C. R. Hebd. Seances Acad. Sci. 1965, 261, 1017-1018.
12. Bolivar, R.A.; Machado, R.; Rivas, C. Acta Sud Am. Quim. 1984, 4, 29-36.
13. (a) Charlton, J.L.; Durst, T. Tetrahedron Lett. 1984, 25, 2663-2666.
(b) ibid. 1984, 25, 5287-5290.
(c) Durst, T.; Kozma, E.C.; Charlton, J.L. J. Org. Chem. 1985, 50, 4829-4833.
14. Meador, M. A., unpublished results.



DIENOPHILE	n	PRODUCT ^a	R	R'	R''	% YIELD	DEHYDRATION		ANTHRACENE	% YIELD
							PRODUCT	% YIELD		
DMA ^b	10.0	3	--	CO ₂ Me	CO ₂ Me	53	--	---	11	80
Me ₂ Fum ^b	2.2	4	H	CO ₂ Me	CO ₂ Me	80	8	100	11	80
MeAcry ^b	2.2	5	H	CO ₂ Me	H	81	9	100	12	87
Me ₂ Fum ^b	1.0	6	H	CO ₂ Me	CO ₂ Me	34	--	---	--	--
6+MeAcry ^b	1.0	7	H	CO ₂ Me	CO ₂ Me, H	93	10	65	13	50

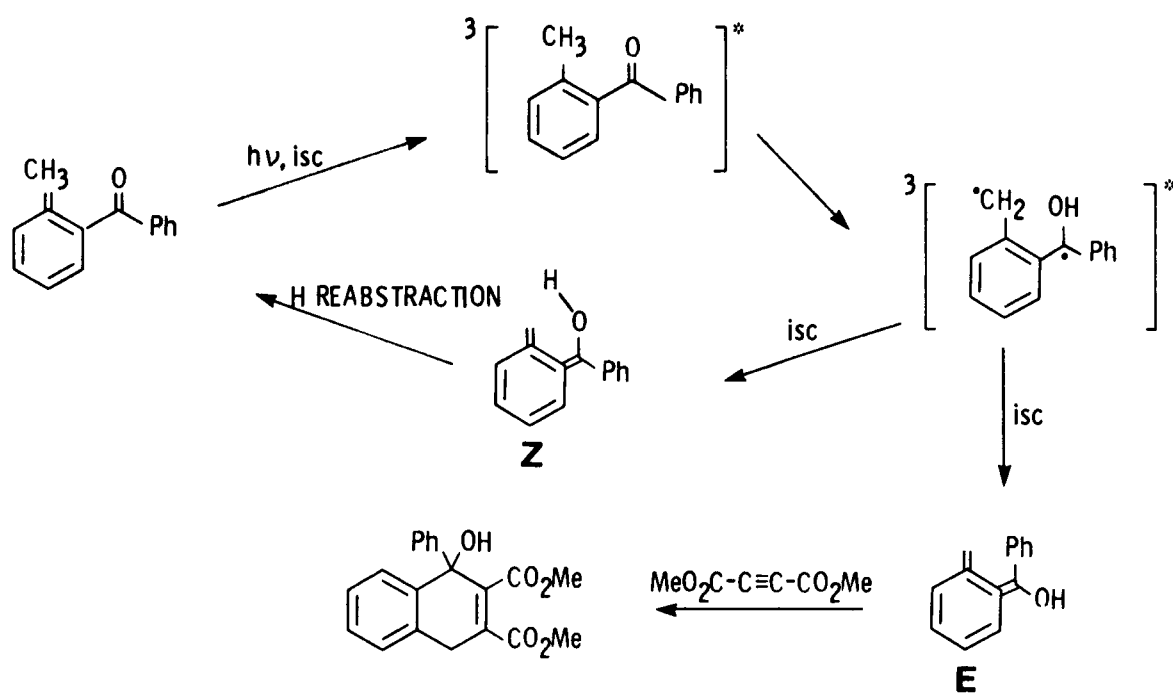
^a25 °C PHOTOLYSIS OF BENZENE SOLUTIONS UNDER N₂ WITH A MEDIUM PRESSURE Hg LAMP EQUIPPED WITH A URANIUM GLASS FILTER.

^bDMA = DIMETHYL ACETYLENEDICARBOXYLATE

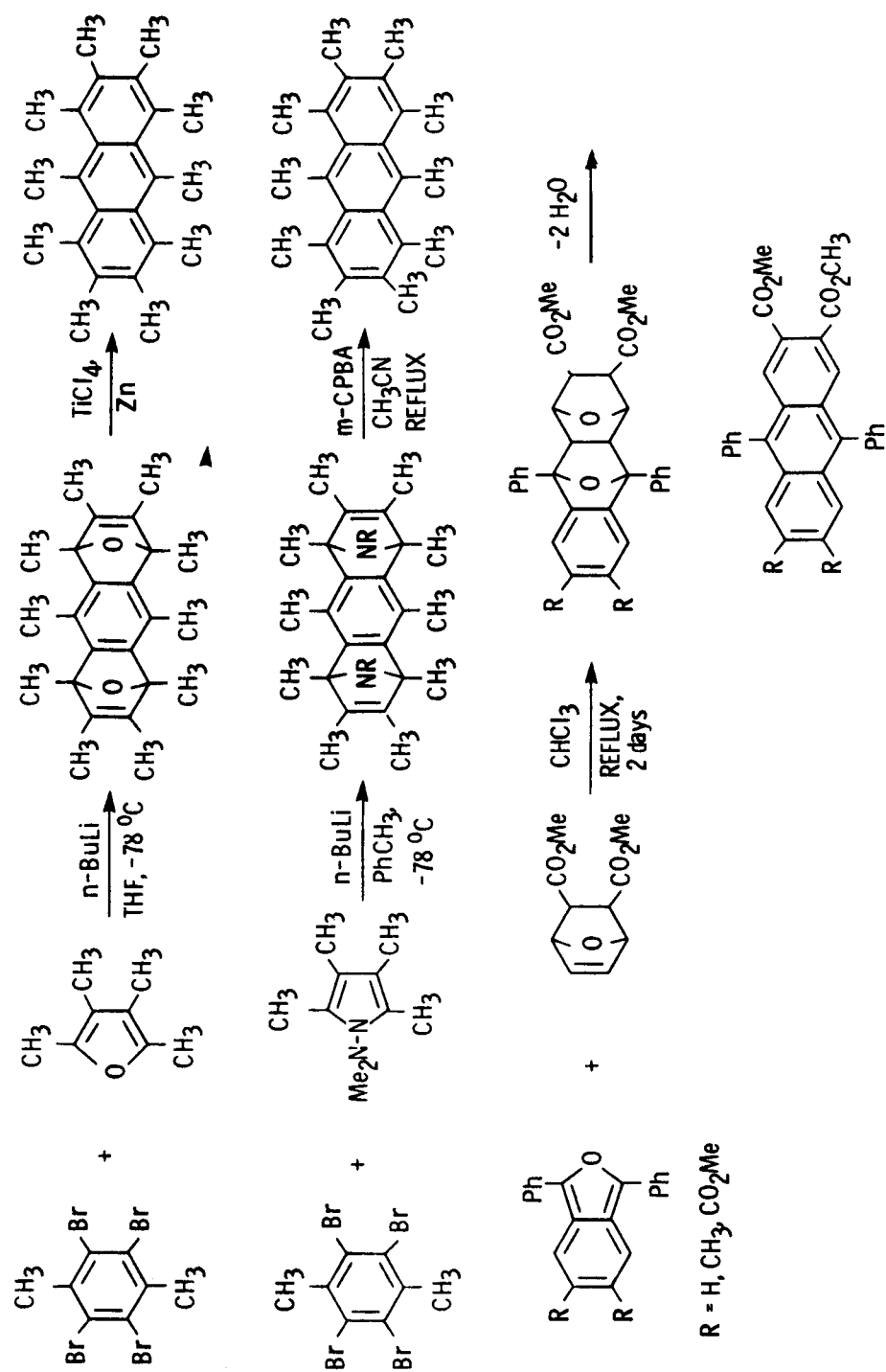
Me₂FUM = DIMETHYL FUMARATE

MeAcry = METHYL ACRYLATE

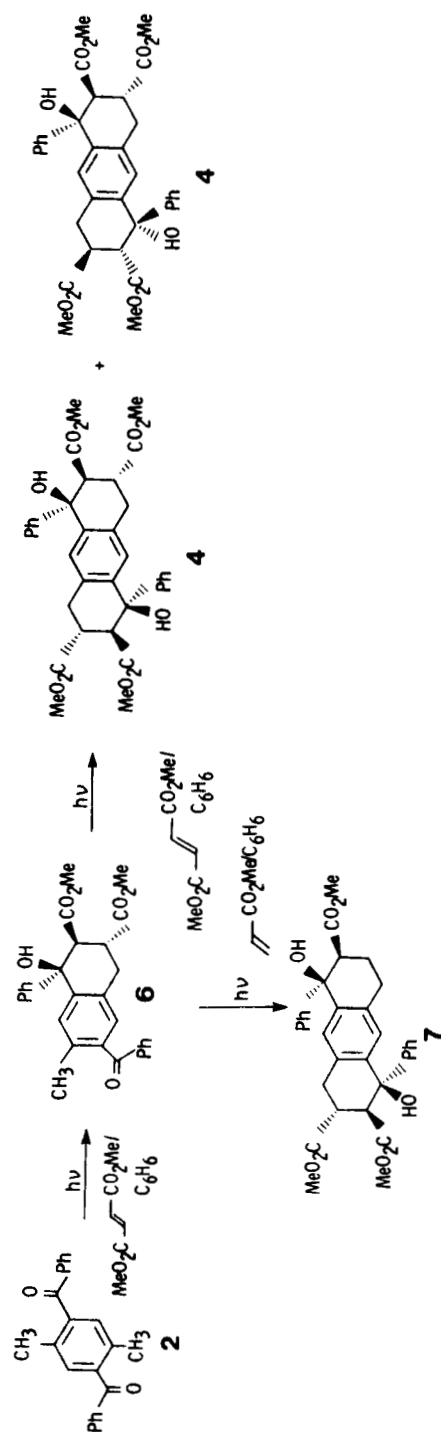
TABLE I



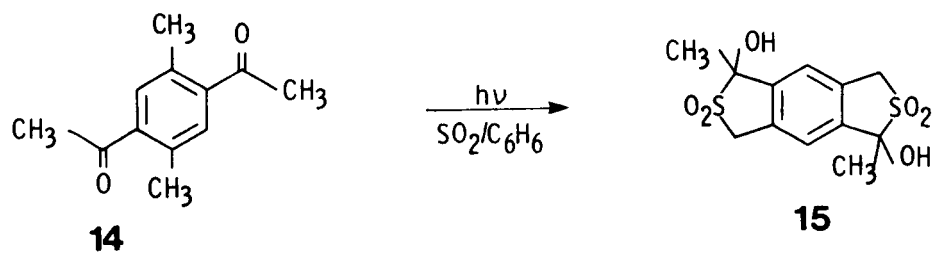
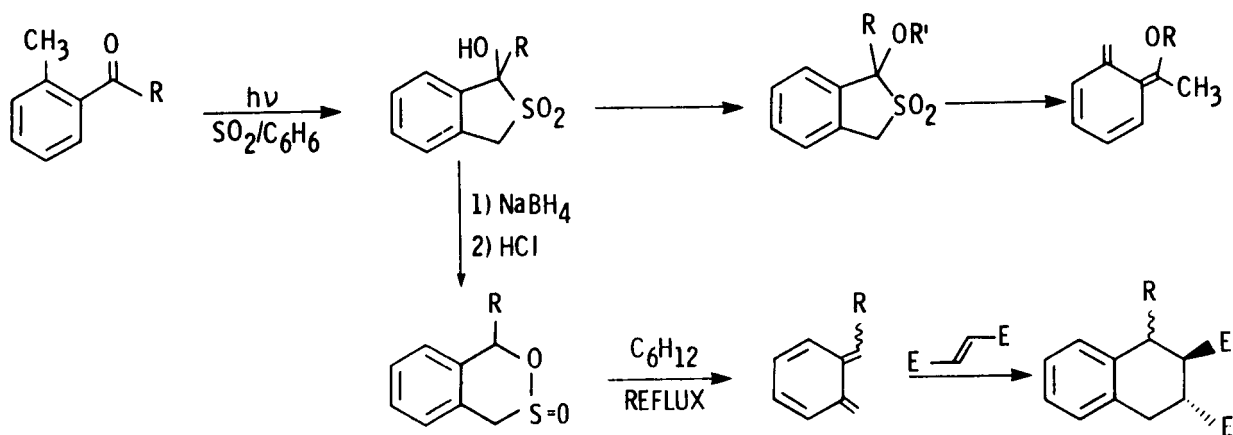
SCHEME 1



SCHEME 2



SCHEME 3



SCHEME 4

1. Report No. NASA TM-89836		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle 2,5-Diacetyl-1,4-Dimethylbenzenes - Examples of Bisphotoenol Equivalents				5. Report Date	
				6. Performing Organization Code 505-63-01	
7. Author(s) Michael A. Meador				8. Performing Organization Report No. E-3493	
				10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the 194th National Meeting of the American Chemical Society, New Orleans, Louisiana, August 30 - September 4, 1987.					
16. Abstract The photochemistry of 2,5-dibenzoyl(DBX)-and 2,5-diacetyl-1,4-dimethylbenzene (DAX) has been investigated. Both compounds readily undergo photoenolization similar to o-alkylphenyl ketones. However, unlike o-alkylphenyl ketones DAX and DBX are each capable of undergoing two tandem photoenolizations. Photoenols derived from o-alkylphenyl ketones have been successfully trapped with Diels-Alder dienophiles to provide a convenient synthesis of substituted tetralins. Similarly, Diels-Alder trapping of DBX photoenils afforded substituted tetra- and octahydro anthracenes. Further manipulation of these photoadducts provided the corresponding anthracenes in good yield. The photochemistry of DAX and DBX will be discussed, in particular their use in the synthesis of substituted anthracenes.					
17. Key Words (Suggested by Author(s)) Photochemistry; Anthracene; Ketones; Diels-Alder reactions; Photochemical reactions			18. Distribution Statement Unclassified - unlimited STAR Category 23		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified		21. No. of pages 16	22. Price* A02	